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4-(3-Ammoniopropyl)morpholin-4-ium tetrachloridozincate(II)

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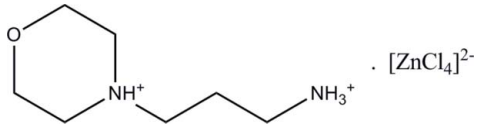
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.019; wR factor = 0.020; data-to-parameter ratio = 19.7.

In the title compound, $(C_7H_{18}N_2O)[ZnCl_4]$, the Zn^{II} ion is coordinated by four Cl atoms in a close to tetrahedral geometry. The crystal packing exhibits C—H···Cl, N—H···Cl and N—H···O hydrogen bonds.

Related literature

For common applications of this material, see: Bringley & Rajeswaran (2006); Tao *et al.* (2003). For structure cohesion, see: Brammer *et al.* (2002). For a discussion of Zn—Cl distances and Cl—Zn—Cl bond angles, see: Guo *et al.* (2007); Valkonen *et al.* (2006). For computational details, see: Prince (1982); Watkin (1994).



Experimental

Crystal data

$(C_7H_{18}N_2O)[ZnCl_4]$
M_r = 353.42
Monoclinic, $P2_1/c$
a = 6.2765 (2) Å
b = 14.3552 (4) Å
c = 15.4858 (6) Å
β = 100.759 (4)°
V = 1370.75 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.55 mm^{-1}
T = 293 K
0.17 × 0.09 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2002)
T_{min} = 0.63, T_{max} = 0.82
13120 measured reflections
3304 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.020
S = 1.04
2696 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O^{i}	0.87	1.95	2.821 (2)	173
N2—H3···Cl2	0.87	2.43	3.209 (2)	150
C1—H6···Cl2^{ii}	0.96	2.72	3.653 (2)	164
C7—H18···Cl2^{iii}	0.95	2.70	3.644 (2)	173
C5—H14···Cl4^{ii}	0.98	2.82	3.657 (2)	144
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C2—H7···Cl1^{iv}	0.97	2.74	3.677 (2)	165

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x, -y+1, -z+1$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2089).

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supplementary materials

Acta Cryst. (2009). E**65**, m282 [**doi:10.1107/S1600536809004346**]

4-(3-Ammoniopropyl)morpholin-4-ium tetrachloridozincate(II)

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Comment

Hybrid compounds have many practical and potential applications in various field (Tao *et al.*, 2003; Bringley and Rajeswaran, 2006). In these materials, the crystal packing is ensured by hydrogen bonds and coulombic interactions (Brammer *et al.*, 2002). Here we report the crystal structure of the title compound, 4-(3-ammoniopropyl)morpholin-4-ium tetrachlorozincate (II) (Fig. 1).

As shown in Fig. 1, to ensure charge balance, the organic species is double protonated at N1 and N2 nitrogen atoms. The structure consists essentially of an 4-(3-ammoniopropyl)morpholin-4-ium and $[ZnCl_4]^{2-}$ anion which are held together by N—H···Cl and C—H···Cl hydrogen bonds so as to build layers developing parallel to (a, c) planes (Fig. 2). These layers, situated at $y = {}^1/_4$ and $y = {}^3/_4$, are themselves interconnected by a set of N2—H···Cl hydrogen bonds (Table 1), alternating with layers, to form a three dimensional infinite network (Fig. 3). The Zn (II) ion is in tetrahedral coordination environment composed of four chloride ions. Each $ZnCl4^{2-}$ anion is connected to its neighbors organic cations, which are associated *via* N—H···O hydrogen bonds, by N—H···Cl and C—H···Cl interactions involving four chlorine atoms (Table 1). The Cl1 and Cl4 are simple acceptors, the Cl3 is double acceptor and the Cl2 is triple acceptor of hydrogen bonds. The (N)—H···Cl distances, varying between 2.42 and 2.54 Å, are smaller than the sum of the Van der Walls radii of the chlorine and hydrogen atoms [*r*(Cl) + r(H) = 2.81 Å]. Consequently, these values correspond well to strong hydrogen bonds.

However, it is worth noticing that the Zn—Cl bond lengths and Cl—Zn—Cl bond angles in the $[ZnCl_4]^{2-}$ anion are not equal to one another but vary with the environment around the Cl atoms(Valkonen *et al.*, 2006). In the title compound, the Zn—Cl bond lengths vary between 2.2486 (4) and 2.2950 (4) Å. The Cl—Zn—Cl bond angles range from 104.32 (1) to 114.43 (2) °. These values indicate that the anionic $[ZnCl_4]^{2-}$ tetrahedron is slightly distorted (Guo *et al.*, 2007).

Experimental

$ZnCl_2$, aqueous 1*M* HCl solution and 3-Morpholinopropylamine in a 1:2:1 molar ratio were mixed and dissolved in sufficient ethanol. Single crystals suitable for X-ray diffraction were prepared by evaporation of a solution of the title compound in ethanol at room temperature after a few days.

Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 and O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

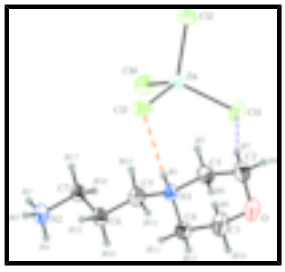

Fig. 1. The molecular structure of the title compound, showing displacement ellipsoids drawn at the 40% probability level.

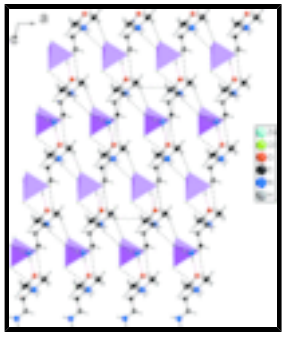

Fig. 2. Crystal structure of (I) viewed along *b* axis showing the layered organization.

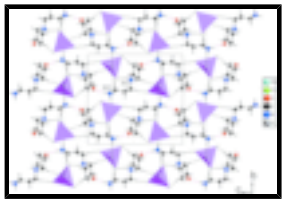

Fig. 3. The packing of (I) viewed down the *a* axis showing layers at $y = {}^{1}/_{4}$ and $y = {}^{3}/_{4}$.

4-(3-Ammoniopropyl)morpholin-4-ium tetrachloridozincate(II)

Crystal data

$(C_7H_{18}N_2O)[ZnCl_4]$	$F_{000} = 720$
$M_r = 353.42$	$D_x = 1.712$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.7107$ Å
Hall symbol: -P 2ybc	Cell parameters from 7336 reflections
$a = 6.2765$ (2) Å	$\theta = 2.8$–$29.2°$
$b = 14.3552$ (4) Å	$\mu = 2.55$ mm^{-1}
$c = 15.4858$ (6) Å	$T = 293$ K
$\beta = 100.759$ (4)°	Block, colorless
$V = 1370.75$ (8) Å^3	0.17 × 0.09 × 0.08 mm
$Z = 4$	

Data collection

Oxford Diffraction XCALIBUR area-detector diffractometer	3304 independent reflections
Radiation source: Enhance (Mo) X-ray Source	2815 reflections with $I > 2\sigma(I)$

Monochromator: graphite	R_{int} = 0.021
Detector resolution: 15.9897 pixels mm^{-1}	θ_{max} = 29.3º
T = 293 K	θ_{min} = 2.8º
φ and ω scans	h = −8→8
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2002)	k = −18→18
T_{min} = 0.63, T_{max} = 0.82	l = −18→20
13120 measured reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.019	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = F /Fmax Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta$F$/6*sigma$F$)^2]^2 A_i are: 8.69 -6.08 5.75
$wR(F^2)$ = 0.020	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.04	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
2696 reflections	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
137 parameters	Extinction correction: Larson (1970), Equation 22
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 64 (4)

Special details

Refinement. Data with I<3σ(I) were excluded from the refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.37044 (3)	0.371470 (11)	0.756164 (11)	0.0273
Cl1	0.48665 (7)	0.47971 (3)	0.85946 (3)	0.0402
Cl2	0.00747 (6)	0.35230 (3)	0.74949 (3)	0.0367
Cl3	0.51658 (6)	0.22854 (2)	0.79921 (3)	0.0372
Cl4	0.43433 (6)	0.42069 (3)	0.62551 (2)	0.0402
C1	0.2040 (3)	0.73398 (12)	0.47182 (11)	0.0383
C2	0.2358 (3)	0.83554 (14)	0.45739 (12)	0.0468
C3	−0.0795 (3)	0.87396 (11)	0.50847 (11)	0.0441
C4	−0.1308 (2)	0.77313 (10)	0.52356 (10)	0.0319
C5	0.0385 (3)	0.61461 (10)	0.54896 (10)	0.0319
C6	−0.1030 (2)	0.58498 (10)	0.61278 (9)	0.0310
C7	−0.0059 (2)	0.60272 (10)	0.70780 (9)	0.0284
O	0.0323 (2)	0.88265 (8)	0.43720 (8)	0.0456
N1	0.07386 (18)	0.71776 (8)	0.54268 (7)	0.0256

N2	−0.1501 (2)	0.56344 (9)	0.76395 (8)	0.0355
H1	0.1513	0.7371	0.5924	0.0370*
H2	−0.0977	0.5758	0.8191	0.0530*
H3	−0.1610	0.5037	0.7569	0.0543*
H4	−0.2786	0.5881	0.7508	0.0540*
H5	0.3391	0.7034	0.4902	0.0478*
H6	0.1254	0.7059	0.4190	0.0461*
H7	0.3247	0.8625	0.5090	0.0563*
H8	0.3080	0.8410	0.4080	0.0566*
H9	0.0095	0.9001	0.5612	0.0534*
H10	−0.2154	0.9071	0.4938	0.0536*
H11	−0.2037	0.7673	0.5727	0.0386*
H12	−0.2185	0.7468	0.4714	0.0373*
H13	0.1820	0.5879	0.5638	0.0378*
H14	−0.0305	0.5963	0.4896	0.0376*
H15	−0.1224	0.5188	0.6059	0.0375*
H16	−0.2428	0.6161	0.5982	0.0365*
H17	0.1334	0.5740	0.7240	0.0348*
H18	0.0068	0.6679	0.7193	0.0354*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02689 (9)	0.02429 (9)	0.02946 (9)	−0.00028 (6)	0.00203 (6)	0.00055 (6)
Cl1	0.0496 (2)	0.03524 (19)	0.03582 (19)	−0.00756 (15)	0.00812 (16)	−0.00963 (14)
Cl2	0.02569 (16)	0.03157 (17)	0.0513 (2)	−0.00010 (12)	0.00342 (14)	0.00177 (15)
Cl3	0.02699 (16)	0.02632 (16)	0.0545 (2)	0.00182 (12)	−0.00201 (15)	0.00397 (15)
Cl4	0.0402 (2)	0.0493 (2)	0.03073 (18)	−0.00006 (16)	0.00604 (15)	0.00497 (15)
C1	0.0350 (8)	0.0496 (9)	0.0336 (8)	0.0016 (7)	0.0147 (6)	0.0046 (7)
C2	0.0456 (9)	0.0538 (10)	0.0415 (9)	−0.0109 (8)	0.0096 (7)	0.0126 (8)
C3	0.0648 (11)	0.0334 (8)	0.0370 (8)	0.0071 (7)	0.0177 (8)	0.0041 (6)
C4	0.0333 (7)	0.0331 (7)	0.0306 (7)	0.0031 (6)	0.0093 (6)	0.0007 (5)
C5	0.0405 (8)	0.0261 (7)	0.0297 (7)	0.0009 (5)	0.0084 (6)	−0.0024 (5)
C6	0.0367 (7)	0.0256 (7)	0.0300 (7)	−0.0060 (5)	0.0047 (6)	−0.0010 (5)
C7	0.0318 (7)	0.0238 (6)	0.0293 (7)	−0.0020 (5)	0.0052 (5)	0.0007 (5)
O	0.0610 (8)	0.0437 (7)	0.0337 (6)	0.0007 (5)	0.0133 (5)	0.0131 (5)
N1	0.0283 (6)	0.0286 (6)	0.0192 (5)	−0.0033 (4)	0.0027 (4)	−0.0002 (4)
N2	0.0441 (7)	0.0331 (6)	0.0310 (6)	−0.0010 (5)	0.0119 (5)	0.0018 (5)

Geometric parameters (Å, °)

Zn1—Cl1	2.2515 (4)	C5—H13	0.966
Zn1—Cl2	2.2779 (4)	C5—H14	0.976
Zn1—Cl3	2.2950 (4)	C6—C7	1.5056 (19)
Zn1—Cl4	2.2486 (4)	C6—H16	0.973
O—C2	1.427 (2)	C6—H15	0.961
O—C3	1.419 (2)	C7—N2	1.4790 (18)
C2—C1	1.494 (2)	C7—H18	0.954
C2—H7	0.966	C7—H17	0.957

C2—H8	0.962	N2—H2	0.875
C1—N1	1.5036 (18)	N2—H3	0.866
C1—H5	0.950	N2—H4	0.869
C1—H6	0.961	C4—C3	1.510 (2)
N1—C5	1.5032 (17)	C4—H11	0.963
N1—C4	1.4922 (18)	C4—H12	0.965
N1—H1	0.875	C3—H9	0.974
C5—C6	1.508 (2)	C3—H10	0.966
Cl1—Zn1—Cl2	107.710 (16)	C5—C6—C7	114.36 (12)
Cl1—Zn1—Cl3	110.593 (17)	C5—C6—H16	109.5
Cl2—Zn1—Cl3	104.316 (14)	C7—C6—H16	109.4
Cl1—Zn1—Cl4	109.501 (17)	C5—C6—H15	106.5
Cl2—Zn1—Cl4	109.997 (17)	C7—C6—H15	107.2
Cl3—Zn1—Cl4	114.428 (17)	H16—C6—H15	109.8
C2—O—C3	109.87 (13)	C6—C7—N2	109.25 (12)
O—C2—C1	110.87 (14)	C6—C7—H18	110.7
O—C2—H7	110.3	N2—C7—H18	107.7
C1—C2—H7	109.9	C6—C7—H17	111.5
O—C2—H8	108.8	N2—C7—H17	108.1
C1—C2—H8	107.1	H18—C7—H17	109.5
H7—C2—H8	109.9	C7—N2—H2	109.7
C2—C1—N1	111.48 (13)	C7—N2—H3	110.2
C2—C1—H5	111.0	H2—N2—H3	109.4
N1—C1—H5	106.6	C7—N2—H4	110.5
C2—C1—H6	110.1	H2—N2—H4	108.0
N1—C1—H6	107.0	H3—N2—H4	109.0
H5—C1—H6	110.5	N1—C4—C3	109.92 (13)
C1—N1—C5	107.86 (11)	N1—C4—H11	108.4
C1—N1—C4	109.72 (11)	C3—C4—H11	110.6
C5—N1—C4	113.91 (11)	N1—C4—H12	107.1
C1—N1—H1	107.7	C3—C4—H12	110.5
C5—N1—H1	108.7	H11—C4—H12	110.3
C4—N1—H1	108.8	C4—C3—O	110.79 (13)
N1—C5—C6	115.63 (11)	C4—C3—H9	110.1
N1—C5—H13	105.3	O—C3—H9	109.2
C6—C5—H13	111.7	C4—C3—H10	107.7
N1—C5—H14	104.5	O—C3—H10	108.4
C6—C5—H14	109.2	H9—C3—H10	110.5
H13—C5—H14	110.3		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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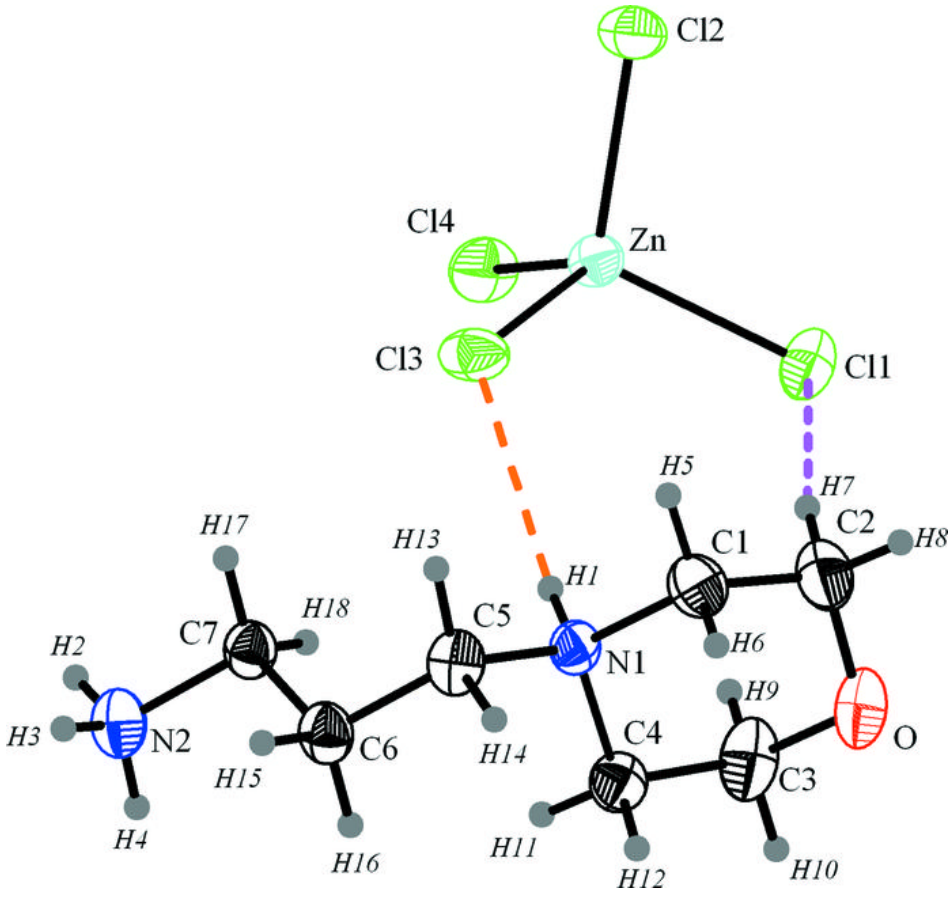
Fig. 1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Cl4
Zn
Cl3
Cl1
H5
H7
C2
H8
H17
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C1
H1
H18
C5
C7
H2
N1
H6
H9
C4
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H3
N2
C6
H14
H15
C3
H4
H16
H11
H12
H10

Fig. 2

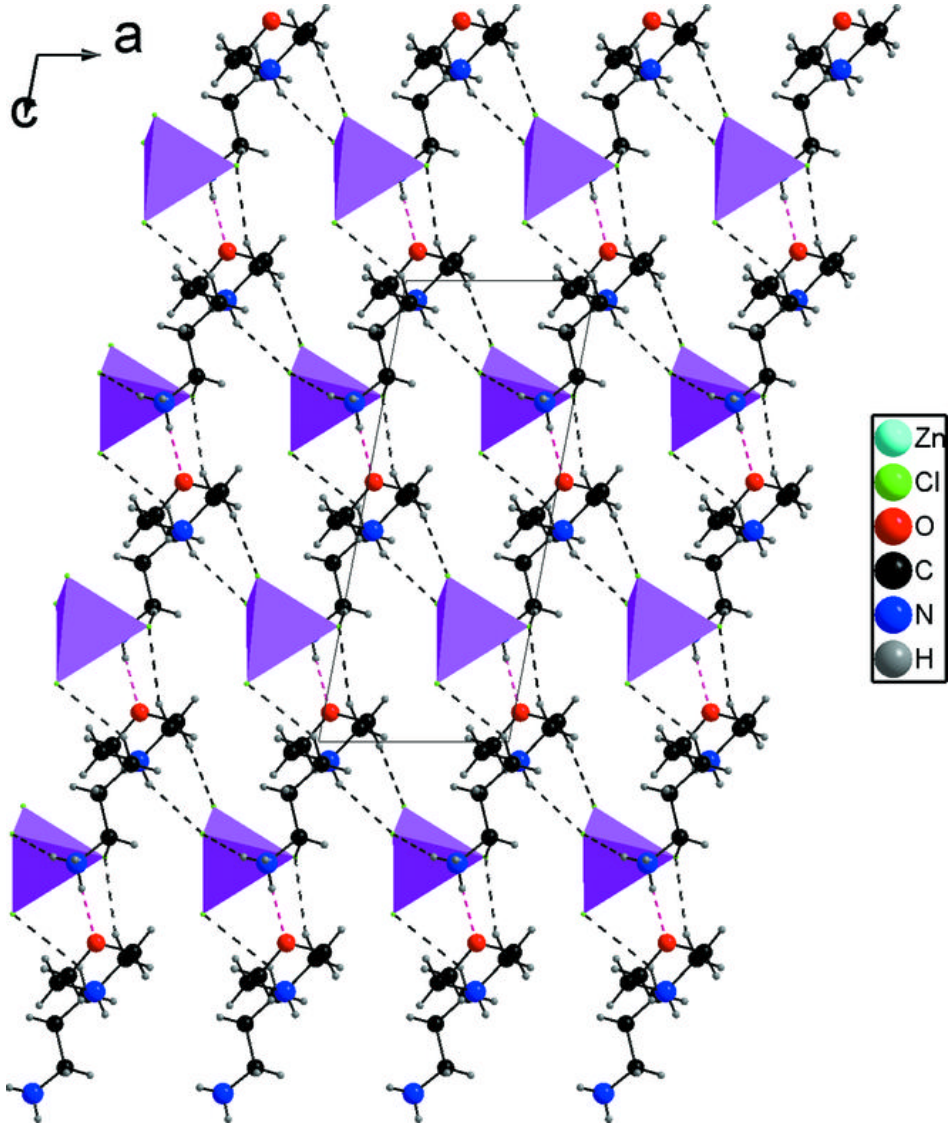

Fig. 3